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FABRICATION AND EVALUATION OF NEW RESINS

VOLUME II: FABRICATION AND EVALUATION

SRI International
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April 1978

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This technical report has been reviewed and is approved for publication.

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An acetylene-terminated sulfone (ATS) oligomer was evaluated as a composite matrix resin and as a reactive plasticizer (RPS) for use with a polysulfone resin. A high cross-link density acetylene terminated quinoxaline oligomer (SBATQ) was evaluated as a composite matrix resin. The processing characteristics of a new polyimide (Thermid) were briefly checked. Studies included preliminary prepreg and process development, initial mechanical property testing, and evaluation of thermal, environmental, and solvent resistance characteristics, as appropriate.

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FOREWORD

This interim report presents the results obtained during the past 12 months on a study dealing with the fabrication and evaluation of new resins for the Air Force Materials Laboratory, Wright-Patterson Air Force Base, under Contract F33615-76-C-5109, Project 2419/04, "New Polymers to Provide the Basis for Non-Metallic Materials for Aircraft and Missile Structures." This work was administered under the direction of Dr. F. E. Arnold (AFML/MBP), Air Force Materials Laboratory, Air Force Wright's Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio.

This report covers work performed from 30 January 1977 to 30 January 1978 and was prepared by M. G. Maximovich and S. Lockerby. The assistance of O. Bergren in prepreg and composite fabrication and testing is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SECTION I

INTRODUCTION

The Air Force Materials Laboratory (AFML) has developed numerous polymer systems with unique potential for structural adhesive and advanced composite applications. Among these systems are thermally stable polymers, moisture-resistant systems, cryogenic resins, long-flow-time materials, and limited-flow polymers. Unfortunately, these systems have sometimes failed to reach the appropriate development areas where their potential could be fully evaluated. The difficulty lies in evaluating the new resins for composite and adhesive applications when only small samples of uncharacterized polymer systems are available. Systems that are otherwise of value are often discarded because of problems that have little to do with the polymer itself. Most composite and adhesive systems now in use exhibited low mechanical properties and disappointing performance when first evaluated.

The objective of this work is to identify, analyze, and solve the material problems associated with new polymer systems. We strive to avoid pursuing polymers with little potential value, and to avoid discarding systems that promise to fill Air Force needs.

SECTION II

SUMMARY

A. Acetylene-Terminated Sulfone (ATS) Resins

Epoxy matrix composites have been used for many years; glass-reinforced epoxy structures have also been widely used in areas ranging from aerospace to the chemical industry to reactional equipment. With the advent of new high-performance reinforcements, such as boron, graphite, and Kevlar 49, epoxy matrix resins were then used to incorporate these new reinforcing fibers into laminates.

The aerospace industry is particularly interested in these materials, which show great potential for reducing weight and increasing performance of flight vehicles. Hoever, as applications became more sophisticated and more demand was placed on the composite systems, problems associated with environmental stability began to emerge that limited the use of these new composites.

The moisture sensitivity of epoxy matrix systems is one such problem. Extended exposure to high humidity reduces the mechanical properties of cured epoxy systems at elevated temperatures. As a result, aircraft using epoxy matrix composites or epoxy-bonded components must be overdesigned, and so suffer weight penalties. This increases the cost of aircraft and reduces payload, range, efficiency, and overall performance. Service life, fatigue resistance, maintenance cost, and survivability are also adversely affected by moisture sensitivity.

These problems led to a growing interest in developing a resin that would retain the processing, handling, and performance characteristics of epoxies, but would be significantly less sensitive to moisture. One candidate replacement resin is the ATS system. The ATS oligomer has a structure similar to that of commercial polysulfone resins, which exhibit good resistance to moisture;[1] it also exhibits a low viscosity melt phase at temperatures below a reasonably low cure temperature. Figure 1 gives the synthetic route to ATS.

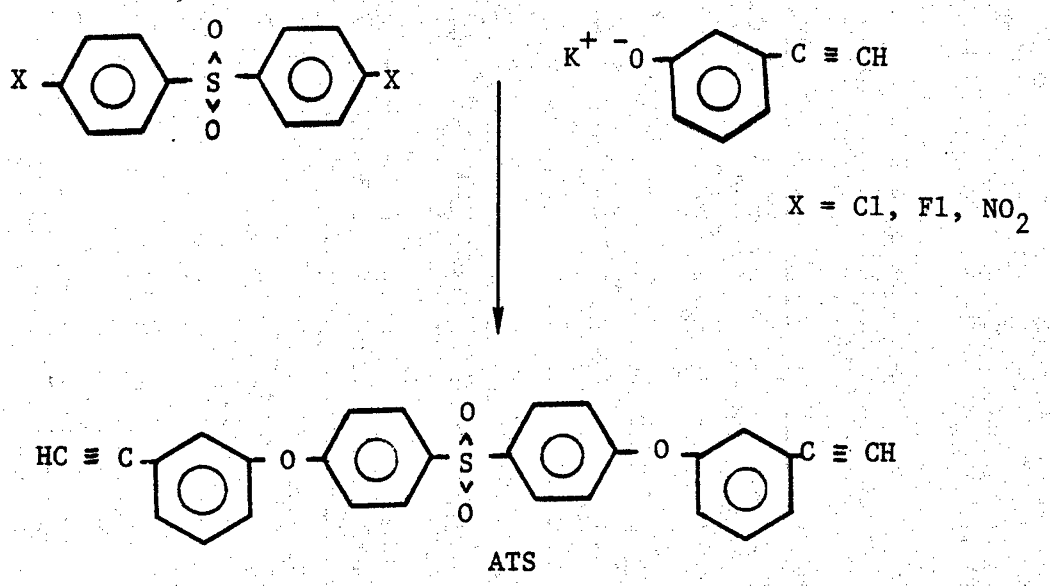


Figure 1. The Synthetic Route to ATS

Our initial work[2] showed that ATS could be readily developed into a composite matrix resin. The resulting graphite-reinforced composite showed potential for improved environmental stability. During the past year, we have fabricated and evaluated graphite-reinforced/ATS laminates as environmentally stable composite materials.

B. ATS as a Reactive Plasticizer (RPS)

Thermoplastic matrix resins have significant potential for reducing the cost of composite structures. Recent studies[3-8] have demonstrated cost saving in the range of 25 to 80% over conventional composites, and often 20 to 40% over aluminum aircraft structure. These savings are a result of novem manufacturing techniques, such as quick consolidation, vacuum forming, postforming, hot stamping, and ultrasonic welding. These processes require seconds rather than the hours required by conventional techniques. Furthermore, thermoplastic matrix resins are tough, and distribute stress well. They offer significant advantages in environmental resistance, and eliminate the need for costly autoclave facilities and slow, expensive

hand layup/vacuum bag manufacturing approaches. However, these materials are not without drawbacks. Processing temperatures are usually 150 to 250 degress farenheit above the glass transition temperature (T_g). Thus, a 350°F service resin system requires a 600°F processing temperature. Additionally, high temperature performance drops significantly at temperatures approaching T_g, limiting the usefulness of the material.

Plasticizers may be used to reduce the processing temperatures of thermoplastics, but they also reduce the end use temperature. A concept suggested by AFML[9] is to use a reactive plasticizer that lowers the T_g of the thermoplastic during processing; then becomes dormant by reacting either with itself or with the host thermoplastic. In the former case, it becomes an inert filler; in the latter, it may raise the T_g of the final material, improving both the processing characteristics and the end-use potential of the host thermoplastic. Work described in this report deals with the use of RPS with a polysulfone matrix to test the feasibility of the reactive plasticizer concept. Performance of the RPS plasticized system is also compared with that of pure polysulfone and a silane-terminated experimental sulfone polymers.

C. High Cross-Link Density Acetylene Terminated Sulfone (SBATQ) As a Composite Matrix Resin

High molecular weight, linear polyphenylquinoxaline (PPQ) polymers synthesized in recent years[10] have shown potential in applications as high temperature adhesives and matrix resins. However, being true high-temperature thermoplastics, they may exhibit thermoplastic yield or failure at temperatures well below the limits set by thermal oxidative stability. The AFML approach, as reported by Arnold and Kovar,[1] was to synthesize acetylene-terminated quinoxaline (ATQ) oligomers, which were expected to offer solubility and processing advantages over analogous polyimide systems[11] and stability advantages over 1,3-dipolar cycloaddition systems.[12] In earlier work,[2] we demonstrated the potential of ATQ oligomers for use as high-temperature structural adhesives.

Other work under AFML sponsorship showed that these oligomers had potential as composite matrix resins. However, high-temperature mechanical

roperties were less than hoped for and thermoplastic failures were still observed. It was postulated that by increasing the cross-link density of the ATQ through the use of an alternative oligomer, single-barreled ATQ (SBATQ), improved elevated temperature performance might be achieved. The work described in this report deals with the fabrication and evaluation of SBATQ as a composite matrix resin.

D. Evaluation of Thermid

Acetylene-terminated polyimides are thermally stable and exhibit potential as matrix resins. Thermid 600, the first commercially available resin of this sort, must be processed from highly polar solvents, such as dimethyl formamide (DMF) or n-methyl pyrrolidinone (NMP). Near the end of this reporting period we obtained and briefly evaluated the processing characteristics of a small sample of an improved Thermid, hot-melt coatable, solvent-free polyimide.

SECTION III

TECHNICAL DISCUSSION

A. Evaluation of ATS as an Environmentally Stable Composite Matrix Resin

The initial evaluation of AS/ATS laminates after environmental aging[2] gave mixed results. The elevated temperature properties retained after environmental exposure were approximately equivalent to those of state-of-the-art epoxies. Better retention had been hoped for, yet these results were encouraging, especially in a new polymer system. Elevated temperature failures were sharp, not thermplastic, and property losses were the same at both ambient and elevated temperatures. Both observations pointed to a mechanism other than plasticization as occurs with epoxies. We began our work, therefore, by analyzing the failures of the earlier specimens and by evaluating new lots of ATS oligomers.

Of the three previously fabricated panels solicited for further study, we chose one for its low resin content (25.5%) and low performance (3825 psi); another, for its medium resin content (32%) and high performance (9160 psi); and the third, for its high resin content (36%) and good performance (7880 psi).

Each panel was C-scanned, and a cross section of each panel was mounted in resin, polished, and studied by optical microscopy (see Figures 2, 3, and 4).

We observed a direct correlation among low resin content, high moisture pickup, and loss of mechanical properties after environmental aging. We postulated, therefore, that extensive fiber/fiber contact occurs, producing resin-poor areas, or voids. These voids provide access to moisture and initiate premature failure.

From the new batch of ATS received from AFML we prepared high quality prepreg, using the optimum techniques developed earlier on this project. An AS/ATS laminate was fabricated, using a modified cure schedule to reduce flow and retain more resin. Only partial vacuum was used below

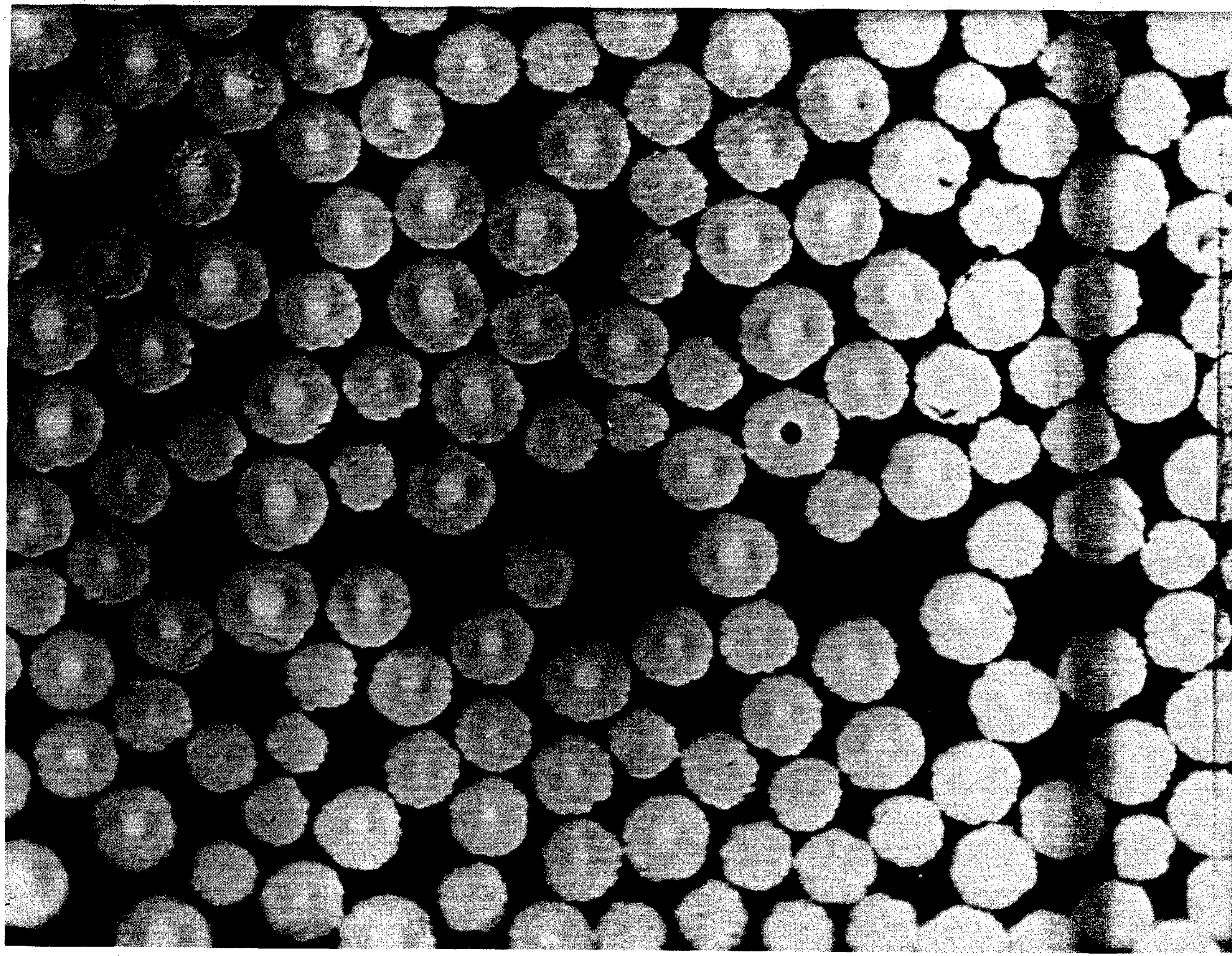


Figure 2: Panel - Low R.C., Low Properties

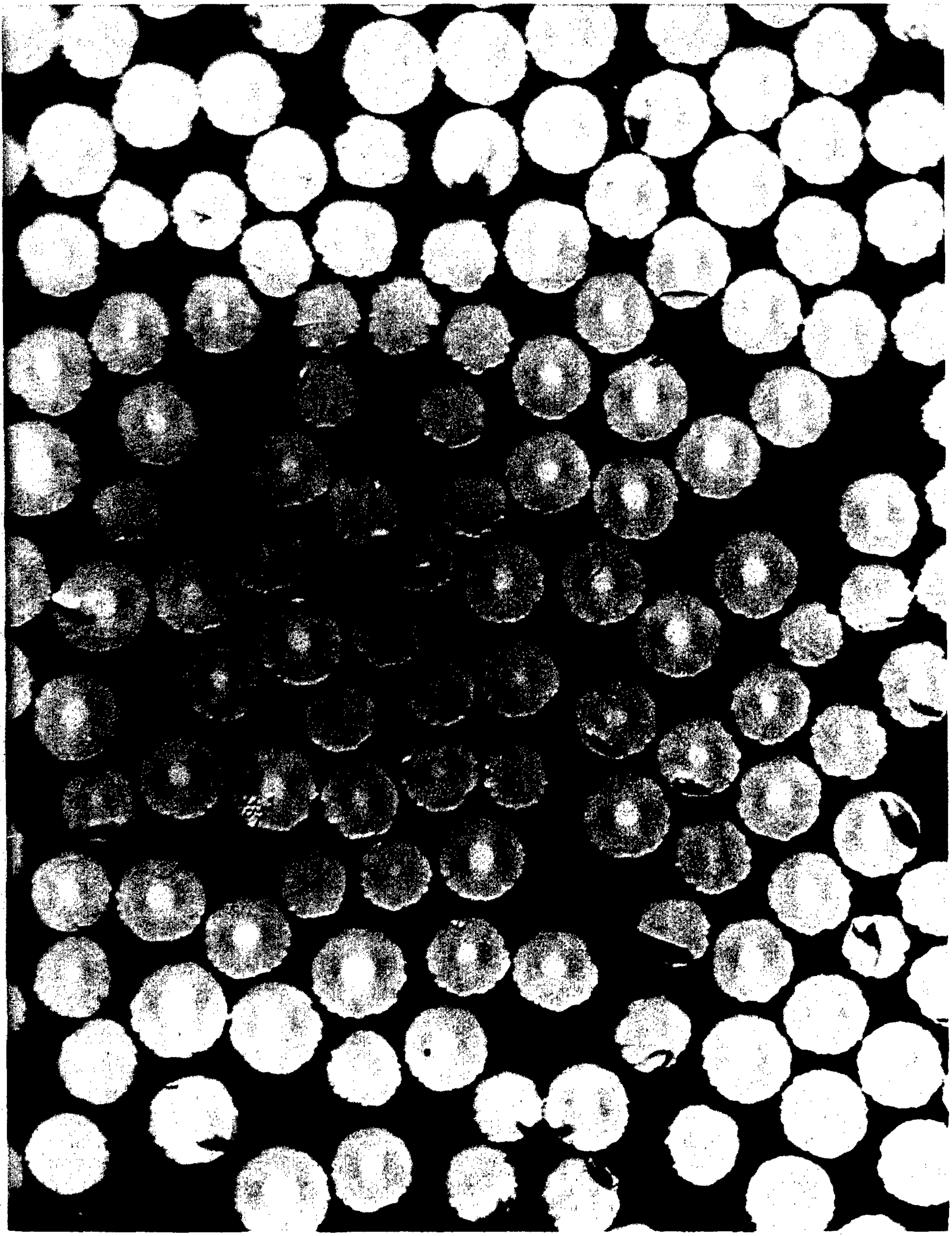


Figure 3. Panel - Medium R.C., High Properties

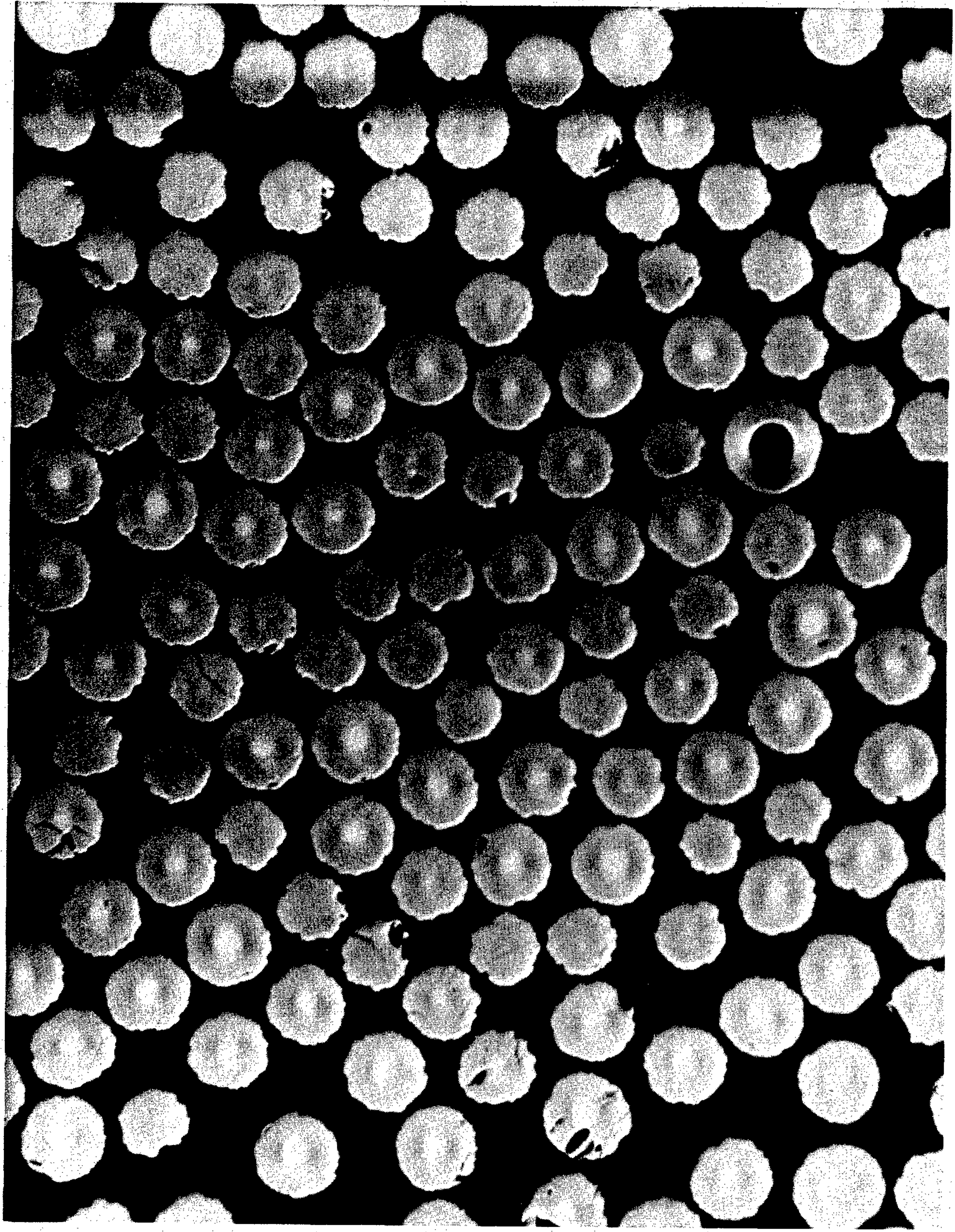


Figure 4. Panel - High R.C., Good Properties

aximum cure temperature. The panel was then postcured overnight at 550°F. The resulting lmainte had a high resin content (44.5%). Optical microscopy (see Figure 5) showed excellent resin/fiber interaction, with no observable voids. C-scanning showed a clear panel with no discontinuities. The new panel, designated 723-91, appeared to be of very high quality by all standards. Table 1 evaluates the panel along with the previously fabricated composite panels used for moisture resistance testing.

The high quality panel was next placed in the environmental chamber at 160°F and 95% RH. Moisture pickup at the pseudosaturation point was determined. Ambient temperature and 350°F short beam shear (SBS) tests were run before and after environmental exposure. Table 2 compares these results with the best previous performance shown by an AS/ATS composite.

Another small batch of ATS was prepregged onto AS fiber, using standard prepregging techniques.

Using the cure cycle (see Table 3) that gave excellent results in earlier work, we fabricated one 4 in. by 5 in. panel from this batch. We observed far more flow during cure than observed with previous laminates. The resulting laminate smelled of uncured resin, and its fibers were barely held together with a fragile, friable matrix. This laminate was discarded as unsatisfactory for testing.

A minilaminate was laid up and an alternative cure cycle (Table 4) was developed to limit the flow. The laminate was then postcured overnight at 550°F. The alternative cure cycle produced a laminate with a short beam shear strength of 7000 psi, which we considered marginally satisfactory. The laminate had a satisfactory resin content and specific gravity; the rather low strength appeared to stem from factors in the ATS.

The remaining prepreg was used to prepare a 4 in. by 5 in. panel for transverse tensile testing, using the Table 2 schedule and postcuring overnight at 550°F. This laminate had a slight odor after curing (perhaps indicating incomplete cure), but the odor disappeared after the postcure. The laminate looked good and had a resin content of 23 wt%.

Two of the four transverse tensile specimens were environmentally aged at 160°F and 95% RH. The pseudosaturation point was reached after 5 days

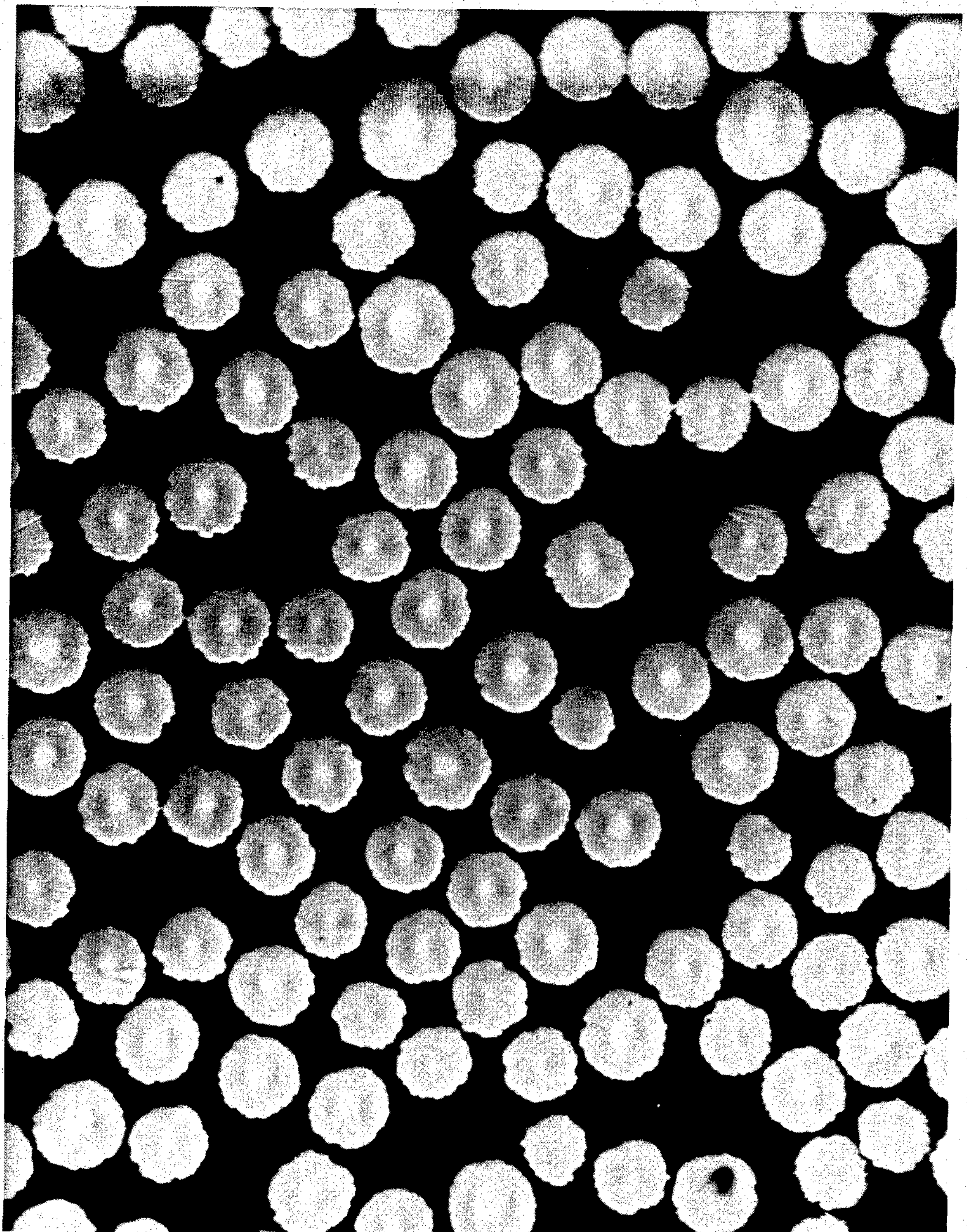


Figure 5. Panel - High R.C., High Properties

TABLE 1

EFFECT OF RESIN CONTENT ON AS/ATS LAMINATES

Specification No.	Resin Content	C-Scan	Optical Microscopy	Ambient Short Beam Shear Strength (psi) (average of 2)
41-2	30.4[a]	Dark	The fibers are too close together; most fibers touch at least four other fibers.	3,925
	25.5[b]			
79-1	32.8[a]		The fibers are too close together, but more resin has infiltrated than in 41-2	9.160
	32.2[b]			
55-1	35.0[a]	Partially clear	The fibers appear well distributed but are packed too closely in some sections.	7,800
	36.2[b]			
91	44.5	Clear	The fibers appear well spaced; few fibers are in contact with other fibers.	12,450

[a] Calculated by weighing lmainate to determine weight loss during processing.

[b] Calculated by resin digestion.

TABLE 2

HUMIDITY AGING OF SELECTED LAMINATES

Specimen	Test Temperature (^{o}F)	Moisture Pickup,[a] Wt% of Laminate	Short Beam Shear Strength,[b] (psi) (average of 2)
723-60	RT	Control	9,030
	350	Control	7,710
	RT	1.2	6,270
	350	1.2	4,830
723-91	RT	Control	12,450
	350	Control	8,500
	RT	0.8	11,350
	350	0.8	6,800

[a] Determined at the pseudosaturation point after 7 to 10 days of exposure to a 160^{o}F, 95% RH environment.

[b] Failures were sharp, indicating no plasticization.

TABLE 3

STANDARD CURE CYCLE

B-Staging	1 hr at 350°F
	Cool
	Vacuum bag, full vacuum throughout
	Heat to 350°F
	Apply 100 psi
	Hold 4 hr
	Cool slowly; use contact pressure

TABLE 4

ALTERNATIVE CURE CYCLE

B-Staging	2 hr at 350°F
	Cool
	Vacuum bag, partial vacuum until 350°F is reached (2 on the gage)
	Heat to 350°F, full vacuum
	Apply 100 psi
	Hold 4 hr
	Cool slowly; use contact pressure

and the water pickup was 1.2 wt% of the laminate. Specimens were tested with no exposure, with full exposure, and finally after they were dried for 4 hr at 350°F following exposure, to evaluate possible irreversible moisture effects. The test results were too low to be meaningful; the matrix was brittle and friable.

A TLC was run on a small remaining sample of the ATS. The chromatogram showed significant amounts of three major impurities not found in previous ATS lots. We hypothesized that the presence of these species could upset the stoichiometry, interfere with the cure, and preclude the successful fabrication of high quality laminates. The composition of this batch of ATS was obviously inferior to and unlike that of all previous ATS batches evaluated at SRI.

A TLC on another ATS batch received from AFML showed the oligomer to be quite pure; significantly better than any preceding batch. We also decided to use Celion 6000 as a reinforcement to see if we could improve mechanical properties.

The ATS showed a higher viscosity during prepregging. The resulting Celion 6000/ATS prepreg showed very little flow or bleedout during cure, quite unlike previous prepreg batches. We postulated that impurities in previous ATS batches acted like plasticizers, resulting in high flow. We also recognized, however, that the use of Celion 6000 reinforcement might be a factor in the reduced flow.

An experiment was deviced to determine if the prepreg flow characteristics were a function of the resin or the fiber and to evaluate the effect of staging on the flow. Layups 1 tow wide, 2 tows high, and 1.5 in. long were made. Five layups were made from the Celion 6000 reinforced prepreg, and one was made with AS reinforcement. The Celion 6000/ATS layups were staged for 0 min, 15 min, 30 min, 45 min, and 60 min, respectively, at 350°F. The AS/ATS layup was staged for 60 min, as was done with previous lots of material at 350°F. All specimens were then cured in the same vacuum bag using the standard cure cycle.

Only two of the six specimens bled at all--the Celion 6000 layups staged for 0 and 15 min. The fact that the AS/ATS sample did not bleed

showed that the flow of this resin sample is much lower than that of previous samples. Table 5 summarizes the results.

TABLE 5

EFFECT OF STAGING ON FLOW OF CELION 6000/ATS PREPREG

	Staging Time at 350°F					Control AS/ATS
Resin Content (wt%)	0 min	15 min	30 min	45 min	60 min	60 min
Before staging	70.5	65.3	77.1	77.9	67.0	75.4
After staging	70.5	61.9	63.0	70.1	67.6	73.8
After cure	34.4	35.7	62.9	70.1	60.6	73.8

We now felt confident that the impurities were indeed responsible for the high flow in ATS. We also suspected them to be responsible for some loss of mechanical properties after environmental aging.

Studies were run to define satisfactory prepreg staging and cure cycles for pure ATS.

We selected a 25-min, 350°F staging cycle to provide a low, controllable flow in the resin. Prepreg was prepared at 39 wt% ATS on Celion 6000, and a minilaminate was laid up, staged, and cured. Little or no flow was observed, but the laminate looked good and the C-scan was clear. The ambient short beam shear strength was 9200 psi, which was also encouraging. A resin digestion test on the final laminate showed a resin content of 38.9 wt %.

We had enough pure ATS left to prepare one full-size laminate for environmental aging of flexural and short beam shear specimens. Enough Celion 6000 reinforced prepreg (resin content 40 wt%) for a $[0°]_8$ layup, 2-5/8 in. by 3-13/16 in., was made and staged for 15 min at 350°F. The laminate was then vacuum bagged and processed using previously developed standard cure and postcure cycles.

The final cured laminate looked good and gave a clear C-scan. Specific gravity was 1.50, with a 34.6 wt% resin content, as determined by resin digestion.

The laminate was then cut into flexural and short beam shear specimens. Half of the specimens were aged at 160°F, 95% RH until apparent saturation point (ASP) was reached. The ASP, determined by plotting moisture pickup versus time$^{1/2}$, was 0.8 wt%. Both aged and unaged specimens were then tested at ambient temperature and 350°F; Table 6 summarizes the results.

TABLE 6

ATS/CELION 6000 LAMINATE PROPERTIES/ENVIRONMENTAL AGING

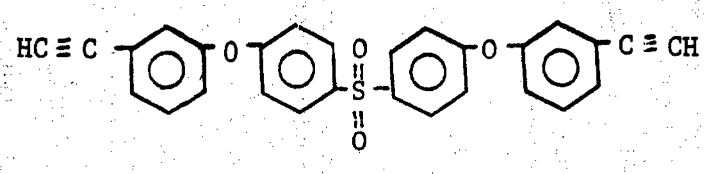
Specimen Condition	Test Temperature (°F)	Flexural Strength (ksi) (single specimen)	% Retention	Short Beam Shear Strength (psi) (average of 4)	% Retention
Control	75	264.4		8625	
	350	195.6		8130	
Aged, 160°F 95% RH	75	172.3*	65.2*	6865	79.6
	350	179.6	91.8	6010	73.9

*Premature failure, possibly because of localized flaws not noticed before testing.

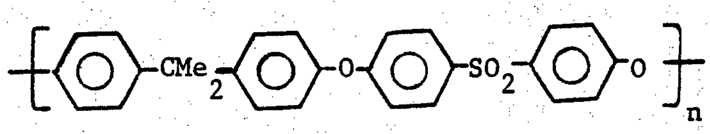
B. ATS as a Reactive Plasticizer (RPS)

A new batch of ATS was received from AFML for evluation as a reactive plasticizer sulfone (RPS). A TLC check showed it to be of very high purity.

We began our evaluation of ATS oligomer as a reactiver plasticizer with Union Carbide P1700 polysulfone. (Figure 6 compares the two structures).



ATS Oligomer



Union Carbide P1700 Polysulfone

Figure 6. P1700 and ATS--Comparison of Structures

A methylene chloride solution of P1700/RPS (4:1, w/w) was made, with a resin solids level of 23 wt%. The low viscosity solution was successfully prepregged onto AS fiber with the Goldsworthy prepregger, using an ambient pot temperature and the rolls at 150°F. The resulting prepreg had good appearance with low tack and drape at room temperature. Resin content was 42 wt% solids with approximately 5% residual $MeCl_2$ solvent.

The T_g of the prepreg was measured as a function of heat staging, using a Du Pont 990 with a 943 TMA attachment in the penetration mode. Table 7 summarizes the study. Prepreg weight loss at the conclusion of the final staging step (1 hr at 500°F) was 4.6 wt%. A series of laminates was then fabricated to define the minimum processing conditions that could be satisfactorily employed. After reviewing the initial T_g data, we attempted to consolidate a small laminate (3 tows wide, 1.5 in. long, 2 plies thick) at 200°F under 100 to 200 psi pressure. The laminate fused, but did not show sufficient flow. Only 2.2% solvent was lost and the laminate was thermoplastic. After an unrestrained postcure

TABLE 7

RPS:P1700/AS PREPREG, T_g AFTER STAGING

Staging Conditions	T_g*	Comments
10 min at 100°F	144°F (62°C)	Resin is white.
+ 2.5 hr at 100°F	147°F (64°C)	
+ 1 hr at 200°F	237°F (114°C)	
+ 1 hr at 200°F	235°F (113°C)	
+ 1 hr at 300°F	264°F (129°C)	Resin beginning to turn gold.
+ 50 min at 350°F	282°F (139°C)	Resin is gold.
+ 2 hr, 40 min at 350°F	295°F (146°C)	
+ 1 hr at 500°F	387°F (197°C)	This T_g is a little higher than P1700 (190°C). The resin is dark amber.

*Determined by TMA with a Du Pont 990 plus a 943 TMA attachment.

for 1 hr at 500°F, the remaining 2.4% solvent was lost, the resin turned from white to amber, and the laminate warped severely and delaminated. Two small laminates (2 in. by 1 in. by 8 plies) were then fabricated and cured under simulated autoclave conditions for 4 hr at 350°F, 100 psi, and full vacuum. Such a cure would be typical for an epoxy (or the pure RPS matrix). They were then postcured for 1 hr at 500°F; one was unrestrained, the other had contact pressure only.

Both laminates appeared sound, all volatiles were removed during the 4 hr, 350°F cure and the laminates remained somewhat thermoplastic after cure. These encouraging results suggested that it might be possible to consolidate, process, and postform the laminate at temperatures of 350°F and higher with standard autoclave or press facilities, and later raise the T_g with an appropriate postcure. However, after the postcure, both laminates were warped; contact pressure was not sufficient to restrain movement. Specimens were cut from both laminates for short beam shear tests. The results are shown in Table 8.

TABLE 8

SHORT BEAM SHEAR TESTS

Laminate	Postcure	Short Beam Shear Strength Average (psi)
A	Contact pressure, 1 hr at 500°F	7280
B	Unrestrained 1 hr at 500°F	5030

Additional prepreg was then prepared and a set of three small laminates was fabricated to determine the efficacy of the following three alternative processing schemes:

C - Vacuum bag only, cure through 500°F

D - Simulated autoclave cure through 350°F, vacuum bag through 500°F

E - Simulated autoclave cure through 500°F

Panels were fabricated, and short beam shear strength, specific gravity, and resin content were determined. Table 9 compares these results with those achieved with the first two laminates. The comparison indicates that pressure is necessary during the postcure.

A T_g determination was run on the laminate cured by schedule E, using a Du Pont 990 with a 943 TMA attachment. The T_g proved to be 394°F, significantly above that of the pure P1700 matrix resin. Schedule E, a simulated autoclave cure through 500°F, gave the best results, producing the laminate with the highest specific gravity (1.56) and short beam shear strength (10,500 psi). This laminate looked good and gave a clear C-scan. Schedule E was therefore used to fabricate a 6-ply, unidirectional laminate, 1-3/16 in. by 4-1/2 in., for environmental aging studies. This laminate also looked good, gave a clear C-Scan, and had a specific gravity of 1.56.

Results of environmental aging studies, however, were disappointing. Short beam shear tests of replicate samples produced erratic results (see Table 10). Moisture pickup of three short beam shear specimens were also erratic. The final weight percent of moisture in the laminate ranged from 0.5 to 1.4:

Specimen	Approximate Duration of Test	Wt% of Moisture
959-84-12	14 days	1.4
-14	9 days	0.7-0.8
-18	1 day	0.5

Both the moisture pickup and mechanical properties indicate nonuniformity in the laminate.

The short beam shear specimens environmentally tested at 300°F and 350°F failed thermoplastically, regardless of aging.

TABLE 9

CURE SCHEDULE FOR RPS-P1700/AS LAMINATES

Schedule	Desceiption	Cure Cycle	Postcure	Avg. SBS (psi)	C-Scan	Specific Gravity	Resin Content %	Comments and Observations
A	Simulated autoclave cure, unrestrained postcure	4 hr at $350^{o}F$ 200 psi	1 hr at $500^{o}F$	5030	-	-	42	Badly warped, poor consolidation.
B	Simulated autoclave cure, contact pressure postcure	4 hr at $350^{o}F$ 200 psi	1 hr at $500^{o}F$ press contact pressure	7280	-	-	43	Slightly warped, some side flow, uneven surface.
C	Vacuum bag only, oven cure	4 hr at $350^{o}F$ 1 hr at $500^{o}F$	1 hr at $500^{o}F$	-	Clear	1.46	36	Not warped, good composition, smooth surface, limited flow.
D	Simulated autoclave cure, vacuum bag oven postcure	4 hr at $350^{o}F$	1 hr at $500^{o}F$	9100	Clear with some striations	1.49	35	Not warped, like C, but with increased flow.
E	Simulated autoclave cure through $500^{o}F$	4 hr at $350^{o}F$ 1 hr at $500^{o}F$	-	10,500	Clear	1.56	34	Similar to D, somewhat increased flow.

TABLE 10

ENVIRONMENTAL AGING OF RPS-P1700/AS LAMINATES

Specimen	Test Temperature	Environmental Aging[a]	Short Beam Shear Strength (psi)[b]	Average	% Retention
959-84-1 -2 -3	RT	no	13,200 12,400 12,600	12,700	-
-4 -5 -6	300°F	no	4,580 7,300 5,290	5,720	-
-7 -8 -9	350°F	no	2,190 1,110 3,680	2,330	-
-10 -11 -12	RT	yes	11,300 9,000 11,200	10,500	82.7
-13 -14 -15	300°F	yes	4,225 3,830 3,820	3,960	69.2
-16 -17 -18	350°F	yes	1,580 700 800	1,050	45.1

[a] 95% relative humidity, 160°F until pseudosaturation point.

[b] All samples tested at elevated temperature showed thermoplastic yield. The load at these temperatures was calculated as the intersection of the initial slope with the slope after yielding.

While the environmental aging was taking place, an experiment was devised to check the quick processing, or post-forming potential of a staged RPS-P1700/AS laminate. Our measurements on the 1:4 mix indicate a T_g of 336°F after processing 4 hr at 350°F. To determine whether this β stage material may be processed like a thermoplastic matrix composite, we prepared a small hat-shaped mold and laid up a 6-ply, unidirectional laminate, 2 in. by 1/2 in. The laminate was cured under vacuum only for 4 hr at 350°F. A press was heated to 370°F (about 35°F over T_g). The consolidated laminate was placed in the mold, but into the press, and heated for 5 min at contact pressure. Pressure was applied slowly. The laminate slid smoothly into the mold. The temperature was raised to 500°F for 1 hr with pressure (200 to 500 psi), raising the T_g to its final value. The part was well formed and showed no fiber breakage. Flow was adequate to fill the corners. This successfully demonstrated the excellent formability of the RSP-P1700 system. Figure 7 shows the postformed hat-shaped specimen.

One of the biggest drawbacks to using P1700 matrix composites is their poor solvent resistance. The matrix dissolves completely in most polar or chlorinated organic solvents. Sections of the RPS-P1700/AS laminate were immersed in a series of solvents at ambient temperature to evaluate their solvent resistance. The specimens swelled in methyl ethyl ketone, acetone, N-methyl pyrrolidinone, meta-cresol, dimethyl sulfoxide, and toluene, and dissolved partially in tetrahydrofuran, chloroform, and methylene chloride. The resin system thus has poor solvent resistance, although it is superior to that of pure P1700 polymer.

To check results and provide comparative data, we decided to fabricate laminates from P1700/AS prepreg and a new silane terminated sulfone from Union Carbide, designated PXKA-6642.

P1700 was successfully prepregged onto AS fiber from a 25% solution in methylene chloride using parameters developed for RPS-P1700. From this prepreg, we made a laminate using the process parameters used to fabricate RPS-P1700/AS laminates (Schedule E, Table 9).

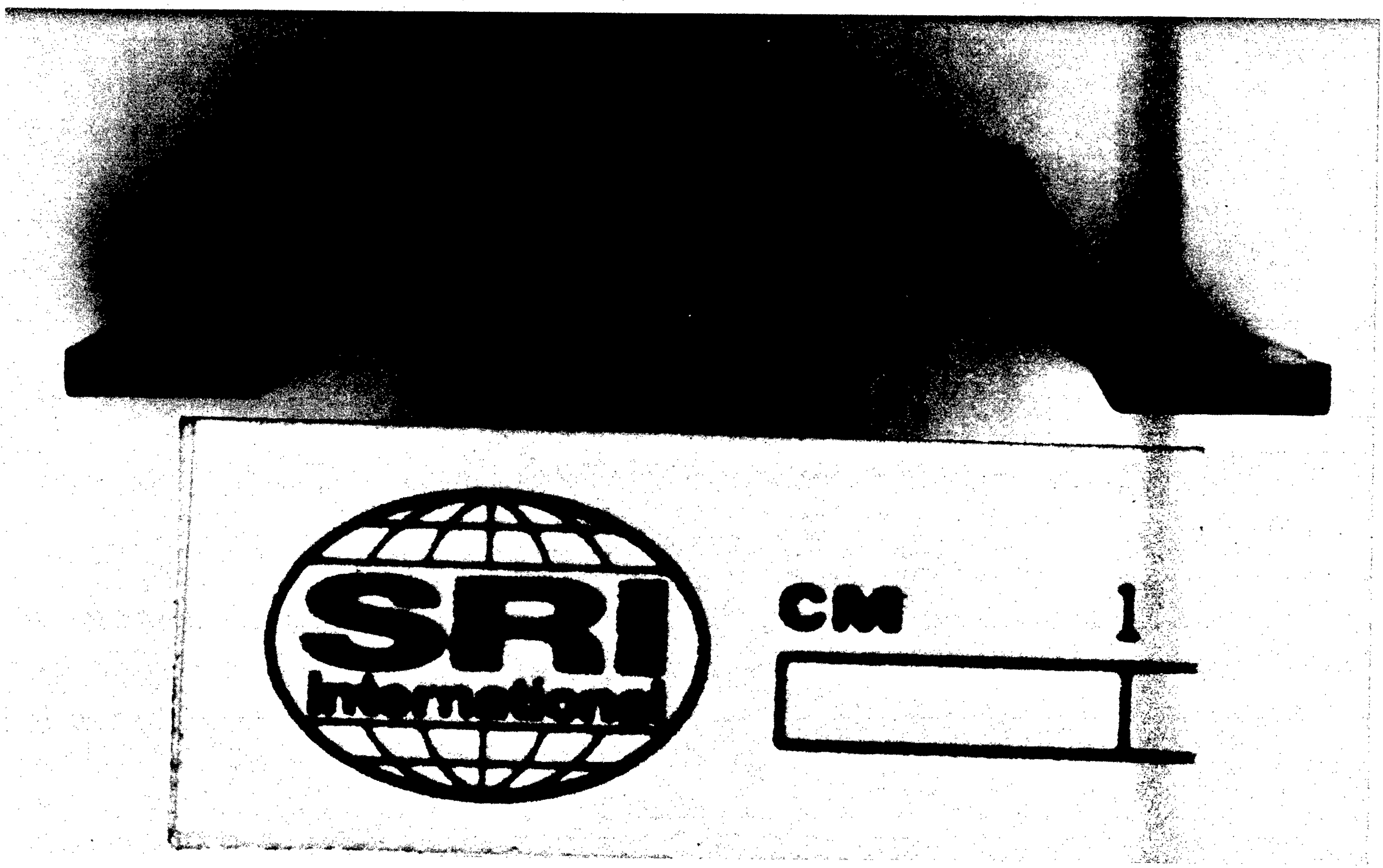


Figure 7. Postformed RPS-P1700/AS Hat Shape

We then compared the moisture absorption of P1700/AS and RPS-P1700/AS laminates. Table 13 follows triplicate specimens through extended environmental aging. The RPS had a positive effect on the laminate; the P1700/AS specimen showed significantly higher moisture pickup throughout the environmental exposure test.

Short beam shear tests were run at room temperature, 300°F, and 350°F for both systems. Though room temperature values were significantly higher for the RPS-P1700/AS laminate with and without environmental exposure, all samples tested at elevated temperatures failed thermoplastically, the resulting data are meaning less and will not be reported here in detail.

Next, we prepregged a 20% solution of PXKA-6642 in methylene chloride onto AS fiber producing a prepreg of good appearance, with apparently satisfactory resin penetration of fiber bundles, but with a low resin content (13 to 18%). Additional solution was added to layups to achieve the desired resin content.

A series of T_g determinations were made after various thermal exposures to define a preliminary cure schedule for PXKA-6642. Table 11 summarizes T_g as a function of heat exposure.

TABLE 11

PROFILE OF PXKA-6642/AS
PREPREG

Heat History	T_g, °F
3 hr at 160°F	379
3 hr at 200°F	379
4 hr at 350°F	381
1 hr at 500°F	396
1/2 hr at 650°F	419

TABLE 13

COMPARISON OF MOISTURE ABSORPTION

P1700/AS Laminate

Time (hr)	Sample	19	66	162	217	282	330	450	477
Moisture[a]	1	.84	.95	1.04	1.06	1.12	1.15	1.22	1.04
Absorption	2	.63	.82	.97	1.16	1.24	1.31	1.29	1.28
Wt% of the laminate	3	.88	1.05	1.34	1.46	1.42	1.61	1.74	1.59

ATS-P1700/AS Laminate

Time (hr)	Sample	19	78	139	210	329	473
Moisture	1	.7	.8	1.1	1.2	1.4	1.4
Absorption	2	.4	.4	.6	.7	.8	.7
Wt% of the laminate	3	.5	.5	.5	.5	.56	.5

[a] Aged at 160°F, 95% relative humidity.

Three laminates were made from the PXKA-6642/AS prepreg. Their cure cycles are shown in Table 12. There is little difference between them. All samples exhibit areas of dry fibers, contributing to erratic short beam shear results. This was surprising, since the prepreg appeared uniform and well wetted out.

TABLE 12

PXKA-6642/AS CURE CYCLES

Cure Cycle	Specific Gravity	Ambient SBS, psi
(1) Heat to 350°F, vacuu, 50 psi	1.46	6580
Hold 4 hr		6590
Heat to 500°F		7230
Hold to 1 hr		8300
Heat to 650°F		
Hold ½ hr		
Cool		
(2) Insert bag into 650°F press	1.47	8705
Apply 100 psi for ½ hr		8200
Cool		7760
(3) Insert bag into 650°F press	1.47	6630
Apply 200 psi for ½ hr		7930
Cool		

We then subjected samples of the PXKA-6642/AS and the P1700/AS panels to solvent tests, using the same series of solvents as for the RPS-P1700/AS laminates.

In all cases, the same solvents attacked the P1700/AS panel and RPS-P1700/AS panel, but swelling or dissolution, or both, was always more rapid or extensive with the P1700/AS panel. The solvent resistance

of the fully cured PXKA-6642/AS panel was significantly better than that of the other two panels, but it was still attacked by methylene chloride, methyl ethyl ketone, and toluene (swelling only). None of the three systems showed adequate solvent resistance.

C. Evaluation of SBATQ as a Matrix Resin

The SBATQ oligomer was synthesized at AFML to offer a high cross-link density version of ATQ with potential for improved elevated temperature performance. Figure 8 shows the structure of SBATQ.

Upon receiving our first lot of SBATQ from AFML, we ran a TLC and found significant impurities. Recalling our earlier problems with ATS, we decided to purify the material before beginning an evaluation.

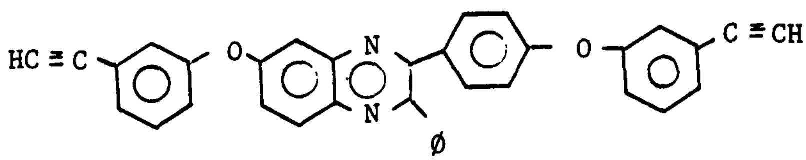


Figure 8 SBATQ Oligomer Structure

The SBATQ oligomer was purified per AFML directions and a DSC was run. The trace correlated well with previous AFML data and confirmed appropriate initial cure parameters.

Hot melt prepregging parameters were next investigated. Pot and banding temperatures of 175°F were required to produce even, high quality prepregged tow on Hercules HT-S fiber. Both appearance and drape were good, but room temperature tack was low. However, laminates were readily assembled and tacked by applying a small amount of heat.

Several small HT-S/SBATQ laminates, 2-ply, 1-1/2-in. by 2 tows wide were made to better define the preliminary processing parameters suggested by DSC testing. A cure cycle or 2 hr at 550°F, under 100 psi pressure, gave satisfactory results:

- Resin color in the bleed-out changed from gold to dark amber but showed no sign of thermal/oxidative degradation
- The ordor of the uncured oligomer disappeared
- The laminate and flash appeared hard and tough, not soft or brittle.

High flow was found, however, necessitating a prepreg staging cycle before fabrication. We therefore flow tested these laminates, as summarized in Tables 14 and 15. As a result of these tests, we selected a staging cycle of 55 min at 350°F to provide optimum flow in future laminate fabrication.

A small HT-S/SBATQ trial laminate, $[0°]_8$, 1-1/2 in. by 5/8 in., was then laid up, staged 55 min at 350°F, bagged, and cured for 2 hr at 550°F, 100 psi. It was then postcured overnight at 550°F. Excessive fiber wash was noted. The first SBATQ/HT-S laminate prepared was of poor quality. The C-scan was dark, confirming that excessive fiber wash had prevented good consolidation. As one would expect, the specific gravity was low (1.45 g/cc). Even with the poor consolidation, however, the ambient short beam shear strength was 8100 psi.

A second laminate was made. The staging time was increased to 60 min at 350°F, and a sealant dam was used to control fiber wash. The standard cure for 2 hr at 550°F and 100 psi plus vacuum resulted in a poorly consolidated laminate with low flow.

We then reevaluated the flow test data and noted irregular flow for all staging times over 45 min. We decided to reduce staging to 45 min and rely on the dam to prevent excessive wash. The resulting laminate appeared well consolidated and had no visible voids.

The laminate was postcured for 6 hr at 500°F in air to completely cure it. The C-scan was clear, the resin content was 31.2 wt%, but specific gravity was quite low at 1.41. Short beam shear tests were run at ambient and elevated temperature (see Table 16).

TABLE 14

INITIAL FLOW TESTS (LARGE INTERVALS)

Minutes of Staging	% Resin Before Staging	% Resin After Staging	% Resin After Cure
0	42.7	41.8	21.8
15	39.9	37.3	20.5
30	49.4	45.9	28.7
45	48.9	45.9	31.3
60	48.3	44.9	35.2

TABLE 15

FINAL FLOW TESTS (SMALL INTERVALS)

Minutes of Staging	% Resin Before Staging	% Resin After Staging	% Resin After Cure
45	43.6	41.5	31.8
50	43.5	41.3	33.8
55	47.3	45.1	37.1
60	47.2	45.3	39.2
65	46.8	42.3	38.5
70	48.0	47.0	45.3
75	44.1	42.6	42.5

TABLE 16

ELEVATED TEMPERATURE SHORT BEAM SHEAR
TESTING OF THE SBATQ/AS LAMINATE

Temperature:	Ambient	450°F	500°F
SBS Strength, psi	8400	6375	4520
	8000	6500	5170
	7530	6100	5430
	7980 average	6325 average	5040 average

These values indicate reasonably good elevated temperature performance, but little if any improvement over the properties expected for regular ATQ matrix materials.

SRI experience has shown that high mechanical properties at elevated temperatures are sometimes difficult to achieve when HTS reinforcement is used. To avoid any potential problem with the reinforcement, we decided to switch to Celion 6000 for future SBATQ work. At this time we received a new lot of SBATQ from AFML. In contrast to previous batches, this one was a solid at room temperature and was hard, not sticky. The resin was prepregged onto Celion 6000, using previously reported parameters developed for AS-reinforced prepreg. The resin became a viscous liquid at 170°F but did not prepreg smoothly. Symtoms were similar to those found when gel particles or unmelted resin are present. The orifice became partially plugged, reducing the resin content of the prepreg. The problem was temporarily alleviated by periodically removing the plug. The cosmetic appearance of the prepreg was good. As in the previous batch, the prepreg had no drape and tack at room temperature, but can be heat-tacked.

Using this prepreg, flow specimens 1 tow wide by 2 tows thick by 1-1/2 in. long were made and run according to the standard SBATQ cure cycle.

Previously, the flow was uniform after 45 min of staging at 350°F and spotty after 60 min of staging at 350°F. In this case, the flow was uniform after staging 30 min, and there was no flow ater 45 min. (See Table 17).

TABLE 17

EFFECTS OF STAGING ON SBATQ FLOW

Minutes of Staging	Resin Before Staging	Resin After Staging	Resin After Cure
0	37.4 wt%	37.4 wt%	25.7 wt%
15	41.3	40.1	26.9
30	41.2	40.0	30.7
45	38.2	37.0	36.7
60	42.2	36.4	36.5

A small trial laminate ($[0°]_{14}$, 9 tows wide by 1 in. long) was made after 30 min of staging at 350°F. Resin solid content was 44 wt%.

The laminate was soft after staging. It was bagged, using sealant as a dam to retard fiber wash, and run according to the standard cure cycle. The laminate showed significant fiber wash despite the use of a sealant dam, but gave a clear C-scan. However, the low specific gravity (1.48) and the resin content (28.9% by digesting) indicate a substandard laminate. Fiber wash may have been a contributing factor. However, the average short beam shear strength of this laminate was 8200 psi; high enough to provide comparative data.

We, therefore, laid up a larger 10 ply SBTQ/Celion 6000 laminate, staged it 30 min at 350°F, cured it according to the standard schedule and postcured it overnight at 550°F. To prevent fiber wash, we wrapped the layup in Armalon. Resin flow was restricted by sealant dams. This laminate had no fiber wash, but resin bleed was greater than desired.

Resin content decreased from 37 wt% in the staged laminate st 25.0 wt% in the final laminate. However, the C-scan was clear and the specific gravity was 1.54, indicating good laminate quality.

Short beam shear specimens were cut and tested before postcure at room temperature and after postcure at room temperature, 450°F and 500°F. (See Table 18).

The balance of the solid SBATQ was prepregged onto HTS using standard prepregging parameters. The resin content was only 30 wt%; therefore, SBATQ/$MeCl_2$ solution was added to increase the resin content to 40 to 42 wt%. (Table 19 summarizes resin flow testing)

TABLE 19

FLOW TEST, SBATQ/HTS PREPREG

Minutes of Staging	Resin Content (wt%)			
	Before Addition*	After Addition	After Staging	After Cure
0	29.8	41.6	38.1	30.7
15	33.2	49.7	46.4	27.6
30	30.3	42.9	38.1	27.2
45	33.3	44.1	40.6	31.7
60	30.2	48.1	44.0	39.1

*Addition of SBATQ/$MeCl_2$ solution to increase the resin content.

The laminate was staged 30 min, then cured and postcured with the standard SBATQ schedules. This laminate was then evaluated and compared with the SBATQ/Celion 6000 laminate (Table 18).

The SBATQ/Celion 6000 was the superior laminate giving higher values at all temperatures. However, these data do not allow a direct comparison of Celion and HTS fibers for use at elevated temperature because of the difference in laminate quality, which is especially evident in the specific gravities of the laminates.

TABLE 18

COMPARISON OF SBATQ/CELION 6000 & SBATQ/HTS

	SBATQ/Celion 6000					SBATQ/HTS			
Specific Gravity:	1.54					1.45			
Resin content[a]:	25.0%					26.1%			
Short Beam Shear:	**Test Temperature (°F)**	**SBS Values**	**Avg.**	**% Retention of RT Prop.**	**SBS:**	**Test Temperatures(°F)**	**SBS Values**	**Avg.**	**% Retention of RT Prop.**
959-95-4	RT	8250	8095		2349-1	RT	7580	7540	
-11		7950			-2		7690		
					-3		7340		
-5	450	7240	7300	90	-7	450	6550	6570[b]	87%
-6		7510			-8		6590		
-7		7150							
-8	500	5930	5960	74	-4	500	5180	5340	1%
-9		6000			-5		5100		
-10		5950			-6		5735		

[a]By digestion

[b]The third specimen here was visibly flawed.

The SBATQ/Celion 6000 appears to be suitable for use at 450°F to 500°F or higher.

D. Preliminary Evaluation of Thermid

We received a small sample of Thermid which is an improved, solvent free acetylene terminated polyimide. Thermid 600, which is commercially available, is difficult to process from the highly interacting polar solvents that must be used with it.

We were asked to fabricate a 5 mil film to check the processability of Thermid. To avoid oxidative degradation, we used a vacuum bag technique. The Thermid powder was placed between Frekote-surfaced Kapton film, next between caul plates, and the assembly was placed into a press at 350°F, then heated to 600°F. After a 2-hr hold at 600°F, the film was slowly cooled under pressure and vacuum. A clear, amber 5-mil film was produced that appeared to be of high quality. It was returned to AFML for evaluation.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

A. Results and Conclusions

1. ATS as a Matrix Resins

The evaluation of ATS as a matrix resin gave highly encouraging results. The combination of epoxy-like processing and high environmental resistance is very attractive. Highlights of our results are:

- Hot-melt coating techniques were successfully developed.
- ATS prepreg showed excellent handling characteristics and cured readily at relatively low temperatures.
- Reasonably good prepreg and laminates were fabricated with minimal difficulty.
- Adequate mechanical properties were achieved with a minimum of difficulty.
- Excellent mechanical properties were demonstrated along with high retention of 350°F properties after environmental aging.

Certainly, some problems should be noted. Care must be taken to synthesize high quality oligomer, to ensure that processing characteristics, mechanical properties, and environmental resistance are not seriously degraded.

2. ATS as a Reactive Plasticizer (RPS)

RPS proved compatible with P1700, and prepreg and laminates were readily fabricated. On the positive side:

- Cured laminates exhibited only 1 T_g value, indicating excellent compatibility
- The T_g of the cured RPS-P1700 system was higher than that of the P1700 alone.
- Solvent resistance was improved
- A β-staged laminate was readily postformed, indicating processability at least equal to that of P1700

- The RPS-P1700 matrix laminates showed significantly lower moisture pickup than those with a pure P1700 matrix.

On the negative side:

- Mechanical properties at 300°F or more were not significantly improved
- Solvent resistance of the RPS-P1700 resin, although superior to that of P1700, was poorer than that of PXKA-6642 silane terminated sulfone and was certainly still unsatisfactory.

3. SBATQ as a Matrix Resin

The SBATQ appears to be a potential high temperature matrix resin. Again, good properties were achieved with relatively little difficulty. Good retention of ambient mechanical properties at 450°F (90%) and at 500°F (74%) was demonstrated, using Celion 6000 reinforcement. SBS values of 6000 psi were also achieved at 500°F with relatively little difficulty.

4. Preliminary Evaluation of Thermid

The small sample of Thermid was readily fabricated into a film. The resin showed adequate melt and flow under normal processing parameters and evolved no volatiles during processing. A high quality film was fabricated with no difficulty.

B. Recommendations

Full development and optimization of the acetylene-terminated sulfone (ATS) resin as an environmentally resistant, high performance composite matrix system was outside the scope of this effort. On the basis of the results of this preliminary evaluation, however, we recommend that such a program be undertaken.

Our evaluation of ATS as a reactive plasticizer (RSP) gave less clear-cut results, but the concept appears feasible and we recommend exploring it further, perhaps with other thermoplastics and plasticizers. Similarly, our results indicate that the SBATQ oligomer system warrants further evaluation as a high-temperature matrix resin, and we recommend further study of the new polyimide Thermid for composite or structural adhesive applications.

REFERENCES

1. Kovar, R. F., and Arnold, F. E., "Polyphenylquinoxalines with Terminal Acetylene Groups", 8th National SAMPE Technical Conference, Vol. 8, 106 (1976).

2. Maximovich, M. G., and Lockerby, S., "Fabrication and Evaluation of New Resins," First Annual Report AFML-TR-77-59, April 1977.

3. Hoggatt, J. T., "Investigation of Reinforced Thermoplastics for Naval Aircraft Structural Applications," Report No. D180-17531-1, May 1973.

4. Hoggatt, J. T., "Study of Graphite Fiber Reinforced Thermoplastic Composites,", Report No. D180-18034-1, February , 1974.

5. Hoggatt, J. T., and Von Volki, A.D., "Evaluation of Reinforced Thermoplastic composites and Adhesives", Report No. D180-17503-3, March 1975.

6. Hoggatt, J. T., "Development of Reinforced Thermoplastic Composites," National SAMPE Conference series, Vol. 20, 606 (1975).

7. Maximovich, M. G., "Development and Applications of Continuous Graphite Fiber Reinforced Thermoplastic Advanced Composites," National SAMPE Conference series, Vol. 19, 262 (1974).

8. May, L.C., and Goad, R. C., "Manufacturing Methods for Fabrication and Assembly of Advanced Composite Primary Aircraft Structure," AFML-TR-75-111, Final Report, July 1975.

9. Kovar, R. F., Ehlers, G. F., and Arnold, F. E., "Reactive Plasticizers for High Temperature Quinoxaline Thermoplastics," AFML-TR-76-28, January 1976.

10. Hergenrother, P. M., Macromol, J., Sci., Revs. Macromol, Chem., C6, 1 (1971).

11. Landis, A. L., Billow, N., Boschan, P. H., Lawrence, R. E., and Aponyi, T.J., Polymer Preprints, 15-538 (1974).

12. Ibid., 533.

☆U.S.Government Printing Office: 1979 — 657-002/06